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## Changes of crystallinity in wood cellulose by heat treatment under dried and moist conditions

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**Abstract** The different effects of heat treatment on wood, especially on the cellulose crystallites of wood under oven-dried and highly moist conditions, were investigated by X-ray diffractometer. Heat was found to increase significantly the crystallinity of wood cellulose; moreover, almost twice as much crystallization was observed after heat treatment of spruce and buna under a highly moist condition than under the oven-dried condition. In pure cellulose almost the same crystallization was observed under both the conditions, whereas more crystallization occurred in wood cellulose than in pure cellulose. Absolute crystallization was observed for the wood species and pure cellulose under both conditions, considering the thermal decomposition of the amorphous region in addition to crystallization. Our results suggested that other components accompanying wood cellulose were involved in the increase of crystallinity by heat treatment, and that wood cellulose contained more quasicrystalline regions than pure cellulose. Moreover, calculated apparent activation energies revealed that crystallization and decrystallization in pure and wood cellulose under heat treatment of highly moist condition were somewhat easier than those under the oven-dried condition. The behavior of the piezoelectric modulus  $d'_{25}$  almost paralleled that of crystallinity.

**Key words** Wood cellulose · Heat treatment · Crystallinity · Activation energy · Piezoelectric modulus.

### Introduction

Wood is subjected to heat treatment for many reasons.<sup>1–4</sup> Heat treatment on wood contributes to thermal degradation of its constituents and changes the crystallinity in wood cellulose. There is evidence that the change of crystallinity

importantly influences the elasticity, absorptive capacity, and other industrially valuable physical properties of the fiber.<sup>5</sup> Researchers have reported on the change of crystallinity of cellulose after heat treatment,<sup>6–8</sup> but all their studies were under an oven-dried condition.

The properties of wood are affected by the presence of moisture during heating. It is assumed that crystallization in wood cellulose might be affected by moisture at the time of heat treatment, and activated energies can give us a clear concept about the effect of moisture. The objective of this study was to determine the different effects on wood, especially on the cellulose crystallites of wood, after heat treatment under oven-dried (OD) and highly moist (HM) conditions. The aim was to explain the effect of moisture in the crystallization process.

### Materials and methods

#### Specimens and sample preparation

Cellulose powder, spruce (*Picea sitchensis*), and buna (*Fagus crenata*) were studied. About 40–80 mesh of wood powder and about 100–200 mesh of cellulose powder (Toyo Roshi Kaisha, Japan) were used in the experiment. To measure the piezoelectric modulus  $d'_{25}$ , the samples were thin rectangular plates with 1.50–1.70 mm thickness cut 45° aslant to the fiber direction. For heat treatment under the OD condition, the cellulose and wood powder were compressed at  $2 \times 10^6$  Kg/m<sup>2</sup> into a 2 cm diameter pallet for 2 min by the pressure gauge. Each sample contained 0.5 g of wood powder. For heat treatment under the HM condition, 1 g of OD wood and cellulose powder were mixed with 3 ml water; 3 ml of water per gram of wood powder was enough to produce the HM condition. After mixing water with wood and cellulose powder, the sample (wood powder plus water) was enclosed in a micro reactor (model SUS316; OM Labtech Co., Japan), which measures the internal pressure and temperature. The internal volume of the micro reactor is 50 ml.

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### Conditions of heat treatment

The samples were dried in a drying oven at 105°C for 1.5h and weighed by an electronic balance after cooling in the desiccator. The heating temperature was controlled at 220°C, 200°C, and 180°C with various durations of heating in a drying oven. The weights of the treated samples were measured after cooling the samples in the desiccator.

Heat treatment under the HM condition was carried out in an oil bath with silicon oil using the same temperature and timing schedule as for the OD condition. The internal pressure and temperature of the micro reactor were measured by a pressure gauge and digital multithermometer attached to the top of the micro reactor. Wood powder was carefully collected from the micro reactor after heat treatment. The heat-treated wood powder was then kept in a desiccator with silica gel about 5 days for preliminary drying. Thereafter, it was dried at 105°C for 1.5h in a drying oven and weighed. The sample was prepared in the same manner.

### Degree of crystallinity and width of crystals determined by X-ray diffractometer

The degree of crystallinity was determined from the ratio of the integral intensity of crystalline portions to the total intensity of the sample over the range from  $2\theta = 5^\circ$  to  $40^\circ$ .<sup>9,10</sup> The relative value of crystallinity  $X/X_0$  was determined from the crystallinity, where  $X$  and  $X_0$  are the crystallinity of treated and untreated wood cellulose, respectively. The width of crystals<sup>11</sup> obtained from (200) diffraction was determined by the following formula:

$$\text{Width of crystal } (t) = K \times \lambda / (B \cos \theta) \text{ (\AA)}$$

where  $K$  is the Scherrer constant (0.9),  $\lambda$  is the wavelength of the X-ray,  $B$  is the half-bandwidth in radians, and  $\theta$  is the Bragg angle.

## Results and discussion

### Pressure and temperature in micro reactor during heat treatment

The internal temperature of the micro reactor took about 45 min to reach the desired level (Fig. 1). The internal pressure of the micro reactor took about 20 min to become constant except during the 220°C treatment (Fig. 2). Whereas the temperature did not vary from the beginning to the end of the experiment under the OD condition, in the case of heat treatment under the HM condition it was not possible to keep the internal temperature of the micro reactor at the desired level from the start of the experiment. The internal temperature of the micro reactor became constant and continue to after 45 min the end of the experiment. Therefore, heat treatments that were less than 45 min under the HM condition were completed before reaching a temperature at the desired level. For our purposes, however,

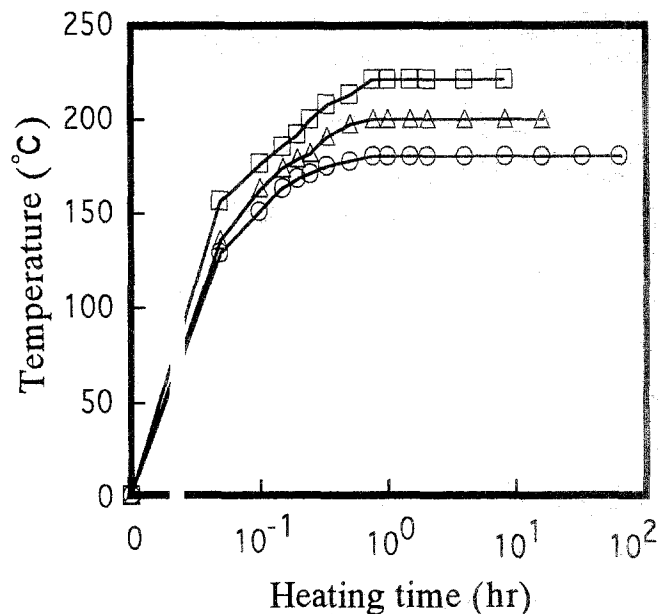


Fig. 1. Inside temperature of micro reactor during the heat treatment under highly moist (HM) condition. squares, 220°C; triangles, 200°C; circles, 180°C

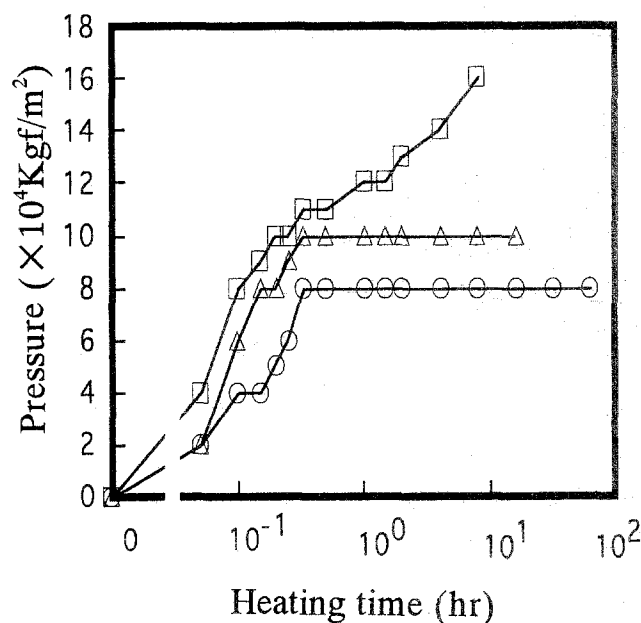
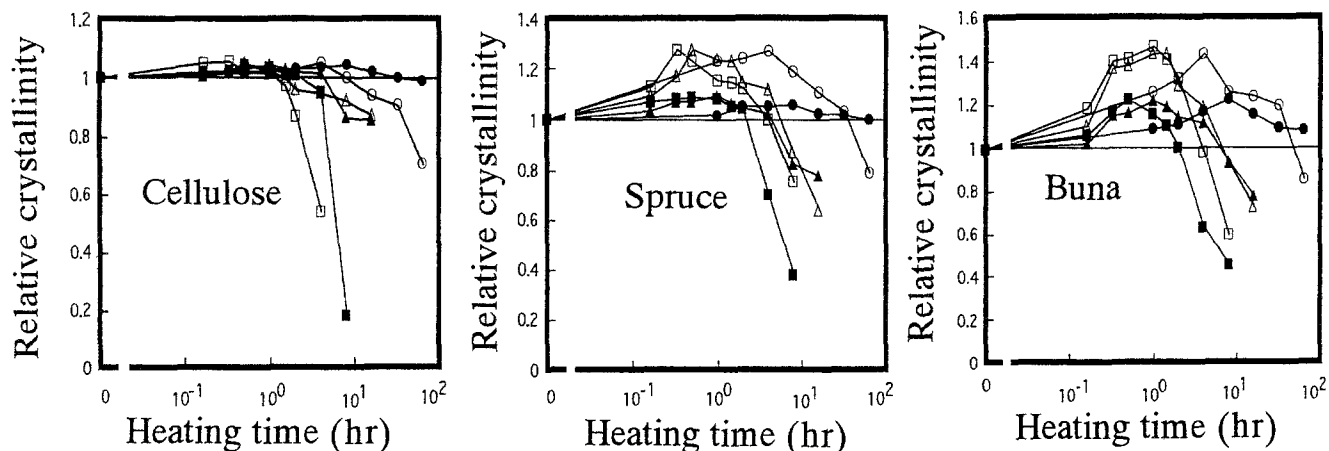


Fig. 2. Inside pressure of micro reactor during the heat treatment under HM condition. Symbols are same as in Fig. 1

the heat treatments (more or less than 45 minutes) were considered to be done at constant temperatures of 220°C, 200°C, and 180°C.

### Degree of crystallinity; absolute values for crystallinity and width of crystal

The degree of crystallinity of the wood species and the cellulose powder increased during the initial stage of heat



**Fig. 3.** Relative value of crystallinity after heat treatment under oven-dried (OD) and HM conditions. Filled symbols, OD; open symbols, HM; squares, 220°C; triangles, 200°C; circles, 180°C

treatment and decreased at the advanced stages (Fig. 3). More crystallization took place in the wood cellulose than in cellulose powder. More crystallization occurred in buna than in spruce. Almost twice as much crystallization was observed after heat treatment of spruce and buna under the HM condition, whereas almost the same crystallization was observed under both the conditions in cellulose powder. Although the internal pressure of the micro reactor varied with the temperature (Fig. 2), maximum values for crystallinity were about the same at all temperatures with various heating times (Fig. 3) under the HM condition. This trend might be due to the lesser effect of pressure on the crystallization process. Therefore, it can be assumed that crystallization is not largely affected by the nonequilibrium pressure during the early stages of the HM condition.

The increase in crystallinity may be explained as crystallization in quasicrystalline of amorphous regions due to rearrangement or reorientation of cellulose molecules inside these regions; the more crystallization in wood cellulose may be due to the crystallization in hemicelluloses and wood cellulose contain more quasicrystalline regions than pure cellulose.

We are currently trying to verify the cause of more crystallization in wood cellulose. There are evidences that xylan and mannan are capable of crystallizing.<sup>12,13</sup> Therefore, in the present study, in addition to crystallization in quasicrystalline regions, crystallization might have occurred in xylan and mannan owing to the heat treatment, which results in more crystallization in wood cellulose than in pure cellulose. At the later stages of heat treatment, the glucosidic linkage is believed to be cut, and depolymerization occurs. In addition to depolymerization, thermal degradation occurs in both the crystalline and noncrystalline regions; and a decrease in crystallinity is observed.

In the case of heat treatment under the HM condition, water becomes steam and produces pressure inside the micro reactor (Fig. 2); hence the inner stress becomes less than in the OD condition. The low stress conditions in the crystalline and amorphous regions would strongly favor crystal-

lization in almost all the quasicrystalline of amorphous region, which is not possible under high stress in the OD condition. There is evidence that activated steam degrades the lignin. Acetic acid forms from the acetyl groups of hemicellulose, and levulinic and formic acids partially form after degradation of the hemicellulose, resulting in partly degraded wood components becoming mobile, which would loosen the inner stress in the crystalline region of cellulose.<sup>14</sup> Under such conditions, the crystallinity of wood cellulose could be increased by the rearrangement or reorientation of the cellulose molecules in the quasicrystalline region. Moreover, after removing some of the acid and all of the acetyl groups, xylan can be induced to form single crystals. Degradation after deacetylation of glucomannan can also form single crystals.<sup>15</sup> Therefore, more crystallization occurred under the HM condition than with the OD condition for both wood species. On the other hand, pure cellulose may contain fewer quasicrystalline regions because it retains a high crystalline state and does not contain hemicelluloses, which effect the rearrangement of cellulose molecules and form single crystals, causing, almost the same crystallization under both the conditions.

When measuring the degree of crystallinity, the effect of a reduction in weight by heat treatment was not considered. At the initial stage of heat treatment there was little reduction in weight, but at advanced stages weight reduction was more apparent. It was then necessary to consider the relative increase in crystallinity due to the decrease in amorphous regions by thermal decomposition, in addition to crystallization. Figure 4 illustrates the ratio of absolute crystallinity ( $X/X_0 \times W$ , where  $W$  is the ratio of residual weight of treated wood/weight of untreated wood), considering the reduction in weight. Variations in the absolute value of crystallinity show a tendency similar to the variation of degree of crystallinity shown in Fig. 3. The absolute increase in crystallinity was also observed after heat treatment of both wood species and cellulose powder under both conditions.

The behavior of the width of the crystals obtained from (200) diffraction under both heating conditions (Fig. 5) was

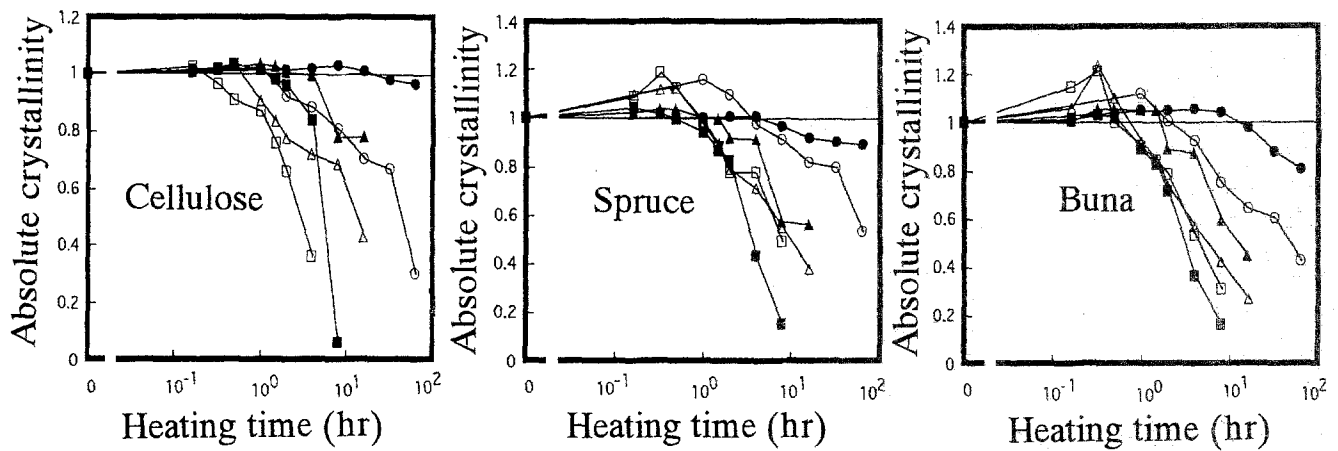


Fig. 4. Absolute crystallinity values after heat treatment under OD and HM conditions. Symbols are the same as in Fig. 3

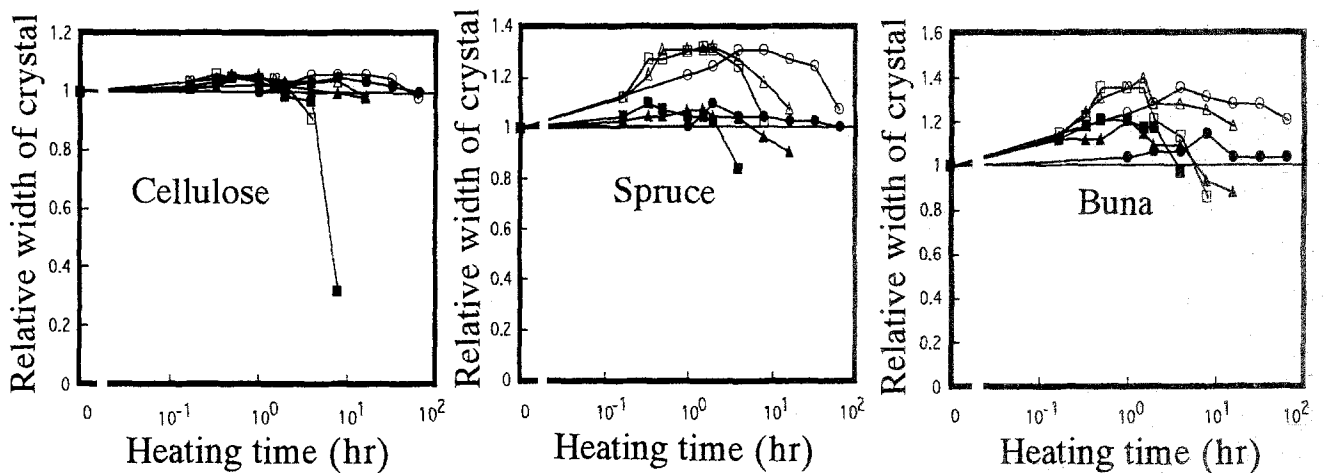


Fig. 5. Effect of heat treatment on the width of crystals obtained from (200) diffraction under OD and HM conditions. Symbols are the same as in Fig. 3

Table 1. Activation energies for heat treatment under OD and HM conditions

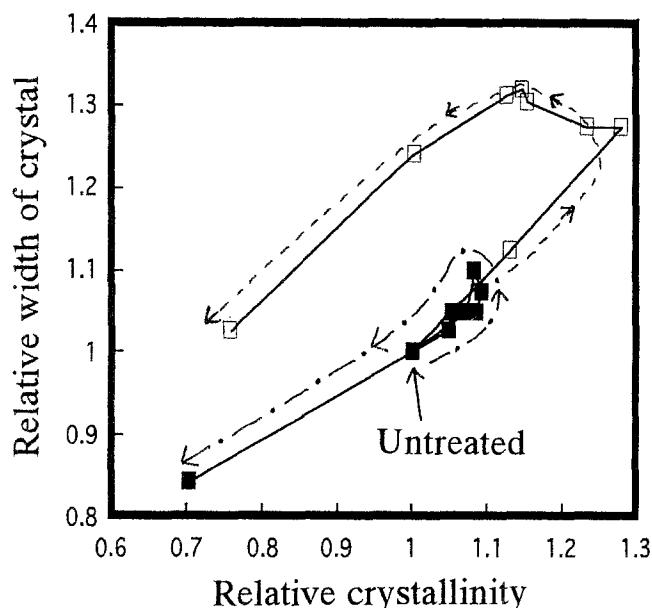
Sample	Activation energy (Kj/mol)			
	Crystallization, OD	Decrystallization, OD	Crystallization, HM	Decrystallization, HM
Cellulose	$2.00 \times 10^2$	$1.83 \times 10^2$	$1.85 \times 10^2$	$1.48 \times 10^2$
Spruce	$2.04 \times 10^2$	$1.79 \times 10^2$	$0.72 \times 10^2$	$1.05 \times 10^2$
Buna	$1.44 \times 10^2$	$1.65 \times 10^2$	$0.92 \times 10^2$	$1.17 \times 10^2$

almost the same as the degree of crystallinity for the wood species and the cellulose powder for the same reason. The changes in the crystallinity of cellulose powder and both species of wood cellulose in terms of the width of the crystals were almost same. The amount of crystallinity relative to the width of the crystals is shown for spruce after treatment at 220°C (Fig. 6). The increase of width of the crystals was similar to the increase in crystallinity, although the decrease in crystal width occurred somewhat later than the change in crystallinity.

#### Activation energies

The apparent activation energies for crystallization and decrystallization of cellulose and both wood species under OD and HM conditions are shown in Table 1. The rates of crystallization  $a$  and decrystallization  $b$  were calculated by the following equation:

$$D_r = \frac{1}{1-C} (1 - Ce^{-at}) e^{-bt}$$



**Fig. 6.** Changes in crystal width relative to the crystallinity of spruce under 220°C heat treatment of OD and HM conditions. *Filled squares*, OD; *open squares*, HM. *Arrows* indicate the direction of effective heating time

where  $D_t$  is the ratio of crystallinity of treated wood/untreated wood,  $t$  is the heating time, and  $C$  is the ratio of the crystallizable amorphous region of untreated wood/total crystalline region.

Activation energy for crystallization and decrystallization was calculated as follows:

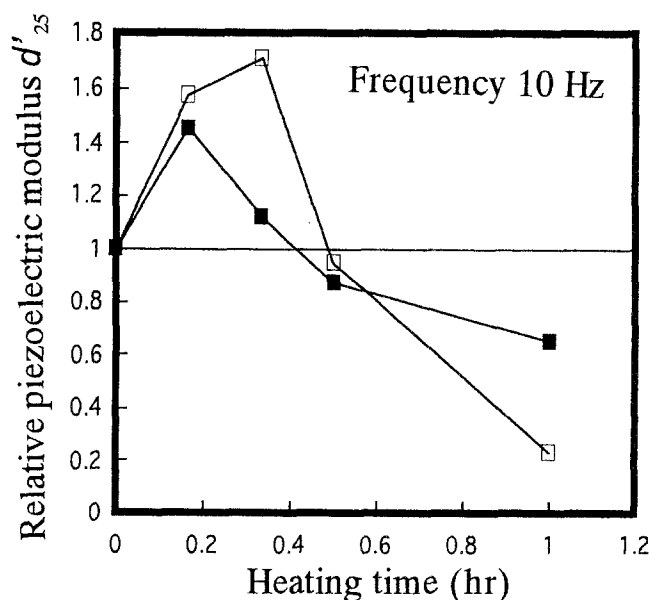
$$a = a_0 e^{-\Delta E_C/RT} \text{ (for crystallization)}$$

$$b = b_0 e^{-\Delta E_D/RT} \text{ (for decrystallization)}$$

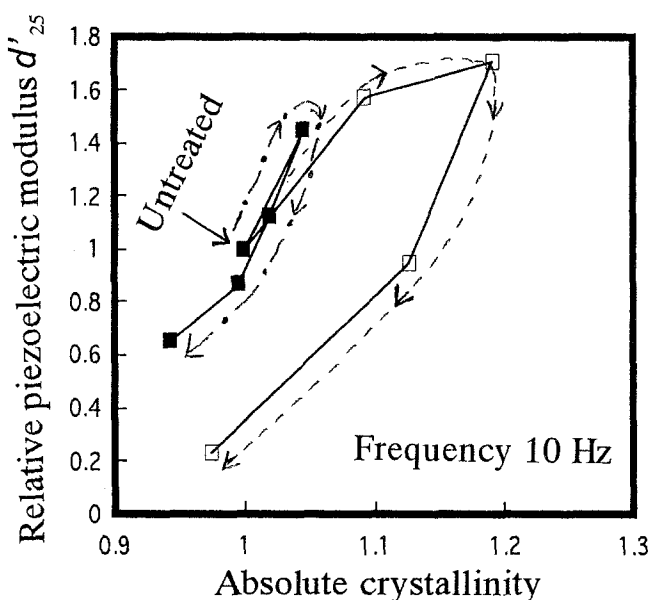
The apparent activation energies for crystallization ( $E_C$ ) and decrystallization ( $E_D$ ) under the OD condition were found to be a little high for pure cellulose and too high for spruce and buna compared with those under the HM condition. Crystallization in pure cellulose and wood cellulose took place more rapidly under the HM condition than the OD condition at all temperatures. On the other hand, decrystallization in pure cellulose at all temperatures and in wood cellulose at 200°C and 180°C took less time under the HM condition than the OD condition. Thus, wood cellulose has a tendency to decrystallize faster under the HM condition than the OD condition at 220°C when the heating time is increased. Therefore, crystallization and decrystallization in pure cellulose and wood cellulose under the HM condition occurred with less activation energy and with somewhat more ease than under the OD condition.

#### Piezoelectric modulus

The piezoelectric modulus  $d'_{25}$  after heat treatment of spruce increased initially and then decreased at later stages, similar to the crystallinity (Fig. 7). Here also, the increase in the piezoelectric modulus was greater after heat treatment in the HM condition than the OD condition. The piezoelec-



**Fig. 7.** Relative value of piezoelectric modulus  $d'_{25}$  after 220°C heat treatment under OD and HM conditions. Symbols are the same as in Fig. 6



**Fig. 8.** Changes of piezoelectric modulus  $d'_{25}$  with absolute crystallinity of spruce after 220°C heat treatment under OD and HM conditions. Symbols are the same as in Fig. 6. *Arrows* indicate the direction of effective heating time

tric modulus greatly depends on the crystalline state. The increase of crystallinity caused the increase of piezoelectric modulus. Therefore, more crystallization in wood cellulose after heat treatment in the HM condition is strongly supported by the results with the piezoelectric modulus. The absolute crystallinity thus coincides with the piezoelectric modulus (Fig. 8). Although the increase in the piezoelectric modulus was almost the same as that of absolute crystallinity, the decrease in the piezoelectric modulus occurred

more rapidly than did that of absolute crystallinity. During the prolonged heat treatment the wood might have developed a fracture in its fibers, resulting in a rapid fall of the piezoelectric modulus compared with the absolute crystallinity.

## Conclusions

This study investigated the effect of moisture on the crystallization process in wood cellulose. The results obtained are as follows.

1. Almost twice as much crystallization was observed in wood cellulose after heat treatment under the HM condition as under the OD condition. This might be due to the easy rearrangement of cellulose molecules and more crystallization in quasicrystalline regions because of low stresses acting in wood components under the HM condition. A larger increase in the piezoelectric modulus was also observed under the HM condition than the OD condition.

2. The crystallinity and piezoelectric modulus increased at the initial stage and decreased at the later stages of heat treatment owing to crystallization of the quasicrystalline region and thermal degradation in both the crystalline and noncrystalline regions. Absolute crystallization was also observed.

3. More crystallization was observed in wood cellulose than in pure cellulose. The results suggest that other components accompanying wood cellulose are involved in the increase of crystallinity after heat treatment, and that wood cellulose contains more quasicrystalline regions than pure cellulose.

4. Based on the calculated apparent activation energies, it can be concluded that crystallization and decrystallization occur somewhat more easily in wood cellulose under the HM condition than the OD condition.

## References

1. Stamm AJ (1956) Thermal degradation of wood and cellulose. *Ind Eng Chem* 48:413-417
2. Kadita S, Yamada T, Suzuki M, Komatsu K (1961) Effect of heat treating condition on the hygroscopicity and dynamic young's modulus of wood. *Mokuzai Gakkaishi* 7:34-38
3. Hirai N, Sobue N, Asano I (1972) Studies on piezoelectric effect of wood. IV. Effects of heat treatment on cellulose crystallites and piezoelectric effect of wood. *Mokuzai Gakkaishi* 18:535-542
4. Fukada E, Date M, Hirai N (1968) Effect of temperature on piezoelectricity in wood. *J Polym Sci* 23:509-517
5. Assaf AG, Haas RH, Purves CB (1944) A study of the amorphous portion of dry, swollen cellulose by an improved thallos ethylate method. *J Am Chem Soc* 66:59-65
6. Fuller CS, Baker WO, Pape NR (1940) Crystalline behavior of polyamides: effect of heat treatment. *J Am Chem Soc* 62:3275-3281
7. Creely JJ, Conrad CM (1962) X-ray diffractometer thermal technique for study of structural changes in cellulosic compounds. *Tex Res J* 32:184-189
8. Conrad CM, Creely JJ (1962) Thermal X-ray diffraction study of highly acetylated cotton cellulose. *J Polym Sci* 58:781-790
9. Segal L, Creely JJ, Martin Jr, Conrad CM (1959) An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Tex Res J* 29:786-794
10. Isogai A, Usuda M (1990) Crystallinity index of cellulosic materials. *Sen I Gakkaishi* 46:324-329
11. Hamed HR, Ueno T, Suzuki K, Toyama N (1995) Preparation of vulcanized fibers and their properties. II. Effect of vulcanization condition on the structure and the strength properties of cotton fiber sheets. *Mokuzai Gakkaishi* 41:399-405
12. Marchessault RH, Liang CY (1962) The infrared spectra of crystalline polysaccharides. VIII. Xylans *J Polym Sci* 59:357-378
13. Yundt AP (1951) Crystalline hemicelluloses. IV. Crystalline mannan. *TAPPI* 34:94-95
14. Tanahashi M, Goto T, Horii F, Hirai A, Higuchi T (1989) Characterization of steam-exploded wood. III. Transformation of cellulose crystals and changes of crystallinity. *Mokuzai Gakkaishi* 35:654-662
15. Timell TE (1965) Wood and bark polysaccharides. In: Cote WA Jr (ed) *Cellular ultrastructure of woody plants*. Syracuse University Press, Syracuse, NY, pp 135-138